

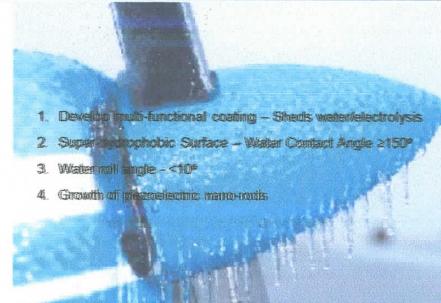
NASA Aeronautics Mission Directorate FY11 Seedling Phase I Technical Seminar
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Nano-Rod Piezoelectrics for Icephobic Surfaces

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Objectives



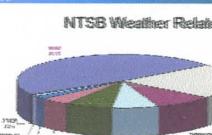
1. Develop multi-functional coating – Sheds water/electrolysis
2. Super-hydrophobic Surface – Water Contact Angle $\geq 150^\circ$
3. Water roll angle - $< 10^\circ$
4. Growth of piezoelectric nanorods

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Weather Related Accidents

NTSB Weather Related Accidents: 1994 - 2003



- 19,562 total accidents
- 4,158 (21.3%) weather related
- 291 (7%) cause by icing

Anti-icing
Preemptive: before the flight enters icing conditions: thermal heat, prop heat, pilot heat, fuel vent heat, windshield heat, and fluid surface de-icers

De-icing
Reactive: ice build up
Includes surface de-icing equipment such as boots, weeping wing systems, and heated wings

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Flight Operations

- **Icing Conditions Disrupt Flight Schedules**
 - Average cost for idling aircraft - \$25/min/minute
 - Flight delays cost the airline industry - \$19 billion/yr
- **On Ground Airframe De-icing**
 - 200-600 million gallons of Aircraft Deicing Fluid (ADF)/yr
 - ADF cost is \$11-\$18/gallon
 - ADF environmental pollutant - 22 million gallons release
 - EPA imposing effluent discharge standards
 - Corrosion of aircraft parts
 - Deterioration of carbon brakes

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Basics of Wetting

Equilibrium Contact Angle
 θ_e : contact angle
 γ_{SL} : solid-liquid surface tension
 γ_{SG} : solid-gas surface tension
 γ_{LG} : liquid-gas surface tension

Young-Dupré relation
 $\gamma_{SV} \cdot \gamma_{SL} = \gamma_{LV} \cos \theta$

Smooth surfaces exhibit maximum contact angles $\sim 120^\circ - 130^\circ$

Wetting Regimes

Hydrophilic $\theta = 0^\circ$	Partially Wetting $\theta < 90^\circ$	Hydrophobic $\theta > 90^\circ$	Super-Hydrophobic $\theta > 150^\circ$
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Basics of Wetting

R. N. Wenzel, 1936
 $\cos \theta_w = r \cos \theta$

θ_w : CA on the rough surface
 θ : CA on the smooth surface
 r : roughness factor ($r > 1$)
Real Area/Flat Area

A. B. D. Cassie, 1948
 $\cos \theta_c = f_1 \cos \theta - f_2$

θ_c : CA on the rough surface
 θ : CA on the smooth surface
 f_1 : fraction of solid
 f_2 : fraction of air ($f_1 + f_2 = 1$)

Surface roughness enhances hydrophobicity

a) Wenzel
b) Cassie

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Super-Hydrophobic Surfaces

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Why Super-Hydrophobic Surfaces

Water Droplet Bouncing

Colin R. Crick - Ph. D. Thesis - University College London - 2011

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Why Super-Hydrophobic Surfaces

Low Roll Off Angles < 10°

Hysteresis $H = \theta_A - \theta_R$
Small Hysteresis
Liquid droplet can roll off easily

Icing

Normalizing Adhesion Strength
Normalized Surface Area ($1-\theta/\theta_{crit}$)
Normalized Contact Angle
 $1 + \cos \theta_{rec}$

Lowers Adhesion Strength

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Super-Hydrophobic Surfaces - Deficiencies

Water Condensation	Frost	WCA Dependency
a)	b)	c)
		Pressure
		Evaporation
Droplet Impact		Droplet Size

Once ice forms – Superhydrophobic surface cannot repel ice growth

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Ice Electrolysis

Petrenko - Dartmouth

Electroplated Copper Grid Electrodes

100 s after 5 watts
 $T = -10^{\circ}\text{C}$

- Small bubbles generated at the interface by ice electrolysis
 $\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$
- Reduces the ice adhesion by 10 times at 21 V @ 30 s.
- AC more efficient than DC

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Innovation Multi-Functional Coating

Super Hydrophobic Surface + Electrolysis Function → Multi-Functional Coating
Provides 2 mechanisms to mitigate icing

Phase I Concept

Piezoelectric Fibers

$2\text{H}_2\text{O}_{(\text{aq})} + 2e^- \rightarrow \text{H}_2 + 2\text{H}_2\text{O}_{(\text{l})}$

Bending Red Ox Red Ultrasonic Vibration

$\text{Ca}^{2+} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Ca(OH)}_2 + 2e^-$

$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$

Energy Harvesting

He et al. - Beijing Nat Lab 7/2011

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ZnO Coating Technical Approach

ZnO Nano-rod Fabrication

Tasks for Phase I:

- Processing/characterization of ZnO nanofibers - completed
- Procurement/equipment development - completed
- Fabricate icing chamber - completed
- Measure contact angles - completed
- Testing office chamber - in progress

Modify optical system for detecting ice formation.

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ZnO Coating

Experimental

Seed Layer	Substrate	Zn Salt	Etchant	T (°C)	Time (min)	WCA (%)	Zn Ratio
Colloidal ZnO	Si	Zn Nitrate	HMDS	90	4	1	
ZnO via Zn Acetate	Si	Zn Nitrate	HMDS	90	4	1	
PVD ZnO	Si	Zn Nitrate	HMDS	90	4,14,72	1,1.25,1.5,2,3	Zn Chloride Zn Acetate
Colloidal Ag	Si	Zn Nitrate	HMDS	90	4	1	
PVD Ag	Si	Zn Nitrate	HMDS	90	4	1	
Carbon Nanotubes	Si	Zn Nitrate	HMDS	90	4	1	
PVD Zn	Si	Zn Nitrate	HMDS	90	4	1	
Colloidal ITO	Si	Zn Nitrate	HMDS	90	4	1	
Stone	Si	Zn Nitrate	HMDS	90	4	1	

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PVD ZnO Seeds

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Colloidal Seeds

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Thermal/Etching/SAMs Treatment

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Lotus Effect

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Carbon Nanotubes

WCA for CNT Coating 143.2°

Metal Coated Substrate 89°

CNT Coating 129°

Metal Catalysis act as nuclei for ZnO Growth

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Mechanical Robustness

Mechanical robustness – poor
•Film fails upon touching
•Films required gentle handling and washing
•Film porosity is needed for super hydrophobic structure

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Phase II

Super Hydrophobic Surface + Electrolysis Function → Multi-Functional Coating
Provide 2 mechanisms to mitigate ice

Improve mechanical properties → Carbon Nanotube/PEDOT:PSS composite
Poly(3,4-ethylenedioxythiophene)- poly(styrenesulfonate)

Printed Electrodes

Super Hydrophobic Electrode Pattern

Goals

- Structure Beads Water
- Structure Sheds Water
- Reduce Power Consumption
- Electrolysis of Ice/Water
- Mechanically Robust
- Easy to Fabricate

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Summary

- Proposed concept for multi-functional coating still valid
- Completed phase I tasks
- Successively Grown ZnO nano-rods
- Successively Characterized Wetting Behavior – 147°
- Environmental Chamber -30°C/Humidity/WCA
- ZnO nano-rods exhibit poor mechanical properties
- Phase II re-focused on mechanical robustness of coating
- Technology – TRL 1 to TRL 2
- Information Dissemination – Conference, Publication

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